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BULLETIN No. 3 OF THE HYGIENIC LABORATORY,
Treasury Department, U. S. Marine-Hospital Service.
WALTER WYMAN, *Surgeon-General.*

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GERMICIDAL AGENT.

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SULPHUR DIOXIDE AS A GERMICIDAL AGENT.

[By H. D. Geddings, Passed Assistant Surgeon, Acting Director Hygienic Laboratory, Marine-Hospital Service.]

In considering the action of sulphur dioxide or sulphurous oxide as a disinfecting or germicidal agent, it is well possibly to begin with a brief review of the nature of the substance, its physical properties, and the method of its action.

Sulphur dioxide, or sulphurous oxide, SO_2, is the only compound of the combustion of sulphur in dry air or in oxygen gas. There are many methods of preparation, the easiest and most simple being the burning of sulphur in air. It may also be prepared by heating copper in a state of fine division as clippings or borings, with sulphuric acid, or by heating sulphur in the presence of concentrated sulphuric acid. By either of these methods a liberal and very regular evolution of the gas is obtained.

Sulphur dioxide is a colorless gas having a peculiar suffocating odor. It instantly extinguishes flame and is totally irrespirable, therefore quickly destroying animal life. It has a density of 2.11; a liter weighs 2.86 grams; 100 cubic inches weigh 68.69 grains. At about 4 atmospheres, or 60 pounds pressure, it can be reduced to a liquid, and at 17.8° C. and at ordinary pressure it is reduced to a liquid condition, colorless, limpid, and very expansible by heat. Cold water dissolves more than thirty times its weight of the gas. Solutions containing sulphur dioxide remain unchanged if excluded from the action of atmospheric oxygen, but when oxygen is present the liquid is rapidly oxidized into a higher form, sulphuric hydrate, H_2SO_4. In a dry state sulphur dioxide and oxygen gases may remain in contact for any length of time without change.

Sulphurous acid, or sulphur dioxide, has active bleaching properties. It is used in the arts for bleaching woven goods and straw. A piece of blue litmus paper plunged into moist sulphur dioxide is at first reddened and then slowly bleached. In considering its action as a disinfecting agent this bleaching property must be borne in mind.

The use of sulphur dioxide as a disinfecting agent dates back to a very remote period, far preceding that of the recognition of the bacterial origin of most contagious and infectious diseases, indeed, going back to the time when the old "humoral" system of pathology was in full vogue; it being supposed, even in the then crude state of knowledge, that "contagion" was a living entity, the destructive effect of the gas was fully recognized. In an old book dealing with nautical matters and intended for the guidance of shipmasters it is related that after smallpox a room or apartment can be rendered safe by burning "a small fragment of brimstone" in the closed apartment. It is the impression of the writer that sulphur is one of the agents mentioned as having been tried in the cleansing of the celebrated Augean stables, prior to the employment of Hercules to complete the stupendous labor. Whether it was burned or whether it was used by other methods is not related. Therefore, sulphur as a disinfecting agent certainly has the respectability of antiquity to recommend it.

There has been much disparagement of the germicidal action of sulphur dioxide when employed for disinfecting or sanitary purposes. It is well to state in the very beginning that the agent has distinct limitations. Certainly it can not be denied that it has great activity when used intelligently and under favorable conditions. Two principal arguments have been actively exploited against the employment of sulphur dioxide, and these are, respectively, its lack of penetrating power and its destructive influence upon fabrics or textiles and tissues. But the question naturally arises, Is penetrating power a prime essential in a disinfecting agent? Take the case of a room or apartment infected by occupancy of one suffering with a contagious or infectious disease. These diseases are usually of comparatively short duration, and are not in any sense of the term lingering or long drawn out. The bedding of the patient may be soiled, but this soiling is more than apt to be superficial, and especially in the case of soiling by fecal matter. Soiling by urinary secretion may, of course, penetrate deeply, but it is fortunate from a sanitary standpoint that the elimination of active pathogenic bacteria by the kidneys is rare, and, indeed, in most diseases admits of some doubt.

A much more serious objection to the employment of sulphur dioxide is its destructive effects upon textiles and fabrics. Being employed, as has already been noted, in the arts as a bleaching agent, it is very evident that it is not adapted for the disinfection of such materials as are colored by vegetable dyes or by most of the aniline colors. The blue dyes of vegetable origin, such as the indigo derivatives, are turned red by the action of sulphur dioxide in the presence of moisture. The red dyes of vegetable origin, such as madder, are converted into a brilliant orange red; nor does the damage stop here. The strength of fabrics thus subjected to moist sulphur dioxide is seriously impaired, and this impairment of strength progresses so long as any of the agent remains in the interstices of the fabric. It is easy to understand this when it is recollected that the hydrated sulphur dioxide is converted into *sulphuric acid* by oxidation, and the destructive effects of this acid upon all fabrics and materials is a matter of common knowledge. Again, cotton or linen fabrics are equally injured, unless the bleaching action is arrested by some appropriate means. The piece of linen or cotton goods, especially if containing starch or size, exposed to the action of damp or moist sulphur dioxide is so acted upon that unless washed immediately after the disinfecting process it will be found to have rotted or decayed in such a manner that it can easily be shaken to pieces.

These are in the main the principal objections to the employment of sulphur dioxide as a germicidal agent and form distinctly one of its limitations. Therefore, let it be laid down as a general rule that, except in the absence of better means, sulphur dioxide should not be employed for the disinfection of fabrics or textiles, or, if so employed, the parties interested should be notified in advance that colored fabrics will probably be changed in appearance, and uncolored ones, unless washed immediately after, may be expected to become useless within a comparatively short time.

But, on the other hand, the agent has most distinct advantages. In the first place, the material for its production is accessible almost everywhere. There is hardly a crossroads store in any part of the country where a reasonable quantity of sulphur, either in the form of flowers or in rolls or sticks under the name of brimstone, can not be obtained. It is an easy matter, therefore, to close an apartment, and in a pot, pan, or other receptacle to burn a quantity of sulphur, and thus render an apartment safe from the danger of conveying infection to those who may subsequently occupy it. Again, the agent is very cheap, and it requires only a comparatively small quantity to disinfect large spaces. Notably is this the case in the holds of ships and in railway freight cars or in other vehicles which are used in the ordinary dispatch of commercial intercourse. For this purpose the agent is most effective and fills an important place in our quarantine and epidemic measures. Whether or not all contagions are air borne is a matter which is yet involved in doubt, but it would seem for practical purposes that they may be so considered. Therefore, wherever infection in its broadest sense has penetrated, conveyed by the surrounding atmosphere, there it is certain that the disinfecting agent, sulphur dioxide, being gaseous in its nature, will penetrate.

From a quarantine and epidemic standpoint it is most fortunate, too, that all the quarantinable or epidemic diseases common to man are caused by simple organisms—that is to say, those which are not of the spore-bearing variety. It will subsequently be shown that as against this class of organisms sulphur is thoroughly efficient when accompanied by moisture and when it can be brought into contact with them. The question of spores introduces another factor into the question, but, as has been said, fortunately the question of spores does not enter into quarantine measures or epidemic practices.

The quarantinable diseases, as defined by the regulations of the Treasury Department of the United States, are cholera, yellow fever, typhus fever, smallpox, plague, and leprosy. To these, from a municipal or sanitary standpoint, may be added the eruptive fevers, measles, chicken pox, scarlet fever, and the dread scorge of municipalities—diphtheria. Leprosy for the present is left out of consideration, for while its causative organism is known its method of contagion or infection is as yet unsettled.

An effort has been made in the experiments that are about to be detailed to establish several points: First, the efficiency of sulphur dioxide as a disinfectant; second, the minimum percentage necessary for efficient disinfection against yellow fever, diphtheria, cholera, and plague; third, to demonstrate the minimum exposure to this minimum percentage in order that disinfection of vessels may be reduced to the smallest possible basis of expense, damage, and loss of time.

Ever since the systematic employment of sulphur dioxide as a germicidal agent it has been empirically recommended that moisture should be present and should be supplied either by the introduction of steam or water in the form of spray, or by water vaporized by the heat engendered in the combustion of the sulphur employed for the production of the disinfecting agent. This matter has been the subject of much discussion, and while generally recognized as being necessary for efficient work, there have been but few authoritative statements on the subject. Therefore, the first experiment made was with a view of solving this question. This was done after the following manner:

PRELIMINARY EXPERIMENT.

A large bell jar having an aperture for the admission of the gas was loaded with envelopes containing strips of flannel which were wet with bouillon cultures of anthrax, cholera, the colon bacillus, typhoid, diphtheria, the bacillus icteroides of Sanarelli, and the bacillus of bubonic plague. The envelopes were sealed and were then perforated with a punch to admit the access of the gas. The bell jar was mounted on a plate of ground glass and air-tight contact was obtained by the use of vaseline. Liquefied sulphur dioxide was the agent employed, and in order to insure its reaching the bell jar in a state of thorough dryness the gas was passed through two drying columns containing pumice stone wet with strong sulphuric acid. The percentage of sulphur dioxide contained in the atmosphere of the bell jar was determined at once by means of the decolorizing action of the gas upon a decinormal solution of iodine and was again determined at the conclusion of the time of exposure. The first experiment showed the presence of 9.8 per cent of dry sulphur dioxide, practically the 10 per cent demanded by the quarantine regulations of the Treasury Department. The time of exposure was forty-eight hours. At the conclusion of the experiment the quantity of gas in the atmosphere had fallen to about 9.2 per cent, showing practically that during the whole duration of the experiment the percentage of sulphur dioxide had been between 9 and 10 per cent. The slips of flannel were then removed from their envelopes and planted into tubes of ordinary buillon, and these tubes were then placed in the incubator at 37° C. and were noted at the end of twenty-four hours. It was then seen that all of the organisms except anthrax had been inhibited. This organism showed a normal growth, apparently not retarded in any way by the process to which it had been subjected. But observation at the end of another twenty-four hours—that is, forty-eight hours in all—showed that the effect on the other organisms had simply been inhibitory and not germicidal. There was a growth in all of the tubes of all of the organisms planted. The question may, therefore, be decided as settled that *dry* sulphur dioxide is *not* an efficient or reliable germicidal agent for quarantine or epidemic practice.

The experiments were then continued as follows:

EXPERIMENT No. 1.

Bouillon cultures of cholera, colon, diphtheria, typhoid, icteroides, and plague were exposed on slips of filter paper inclosed in sealed envelopes, which envelopes were perforated to allow access of the gas. The cubic capacity of the room used was 500 cubic feet. The percentage of sulphur dioxide, by actual determination, was 0.6 per cent. The vessel in which the sulphur was burned was immersed in another vessel containing a quantity of water, which was measured before and after the experiment, and the amount found evaporated was 150 c. c. Time of exposure, twenty-four hours.

Six cultures of each of the above organisms were placed on a shelf within the room; six each were suspended near the ceiling; two were placed on the floor of the room; one of each under a heavy carpet upon the floor.

The temperature at the beginning of the experiment was 31° C., and the highest temperature noted during the continuance of the experiment was 35° C.

The results obtained in this experiment were very uniform. No single organism survived the process. The controls in all cases grew.

EXPERIMENT No. 2.

The next experiment was identical with the preceding, the same organisms being used, except that the percentage of gas was 0.8 per cent and the time of exposure was shortened to twenty hours. The results were the same. All organisms subjected to the process were killed, while the controls all grew.

EXPERIMENT No. 3.

The next experiment was made with cultures as before, disposed upon the floor of the room, the shelf, suspended near the ceiling and under carpet on the floor, but to obtain the effect of the gas upon spores, cultures of anthrax containing spores were exposed under the same conditions. The percentage of gas was 1.6 per cent. One hundred and fifty cubic centimeters of water were introduced into the room, after the combustion of sulphur, in the form of steam. Time, eighteen hours.

The results were that anthrax exposed under all conditions showed a growth. The other organisms were uniformly killed, while all controls showed normal growth.

Experiment No. 4.

Percentage of gas 4.25 per cent; time, sixteen hours. Cultures, anthrax, cholera, colon bacillus, diphtheria, typhoid, icteroides, and plague, were exposed in envelopes upon the shelf, and floor of the room, under carpet, and enveloped under four layers of blanket. Of those exposed on the shelf all were killed. Of those exposed under the carpet anthrax grew while the others were uniformly killed. Of those enveloped in the blanket anthrax, typhoid and icteroides grew; cholera, colon, diphtheria, and plague, were killed. Controls to this experiment grew uniformly.

In the experiments involving the use of a small percentage of gas spore-bearing organisms, as anthrax, were not employed, the design being to observe the effect of low percentages of the gas upon organisms interesting from a quarantine or epidemic point of view. The results would seem to indicate that provided a proper quantity of moisture be present, even these low percentages are efficient against ordinary pathogenic organisms.

Numerous experiments have been made with various percentages of the gas to fulfill the third indication laid down for these experiments, namely, to demonstrate the minimum exposure to minimum percentage.

The results of these experiments have been uniformly to show that, while low percentages of the gas have been uniformly efficient as a disinfecting agent, it has been found impossible to produce germicidal effects within any very short period. The times tried have been, respectively, two hours, four hours, six hours, eight hours, twelve hours, fourteen hours, and sixteen hours. Sixteen hours, as has been shown above, have given good results with comparatively low percentages of gas, but uniform germicidal effects have not been obtained under this time. This would seem to indicate that a certain time is necessary to allow the gas to penetrate and remain in contact with the organisms which it is designed to destroy, but, above all, the experiments have demonstrated that it is possible to employ the gas as a germicidal agent in much lower percentages and for considerably shorter term of exposure than is now required by the regulations of the Treasury Department of the United States. Four and one-quarter per cent has been the maximum quantity of gas used; twenty-four hours the longest time. While the time may have been shortened materially by the employment of this percentage, it is still believed that twenty-four hours should be the minimum time.

Now let us see what practical bearing these results may have upon quarantine practice. The regulations require for the holds of vessels, either iron or wood, 10 per cent volume of gas, and forty-eight to seventy-two hours' exposure in the case of wooden vessels; twenty-four to forty-eight hours in the case of iron vessels. This percentage of gas can only be obtained by the use of special apparatus in the nature of a specially constructed furnace and a fan or blower driven by an engine to aspirate the gas from the furnace as fast as formed and introduce it into the hold of a ship undergoing disinfection. Investigation of many quarantine stations has demonstrated that in none of them was 10 per cent sulphur dioxide used. In many of them the percentage ranged from 2.50 to 6 per cent. So far as the record shows there is no instance of a ship once having undergone disinfection at a national or State quarantine station having imparted the infection of the disease which was principally the subject of quarantine, yellow fever, to any person or to any community subsequently in contact therewith.

It would seem that as a result of these experiments there might be an essential change made in the quarantine regulations upon this point. Five per cent sulphur dioxide intelligently applied for twenty four hours would seem to be all that would be necessary. This percentage of gas, or very near it, can be obtained by the old method of the combustion of sulphur in pots which can be placed in the holds or other apartments of ships which it is desired to disinfect. And the time can be shortened from seventy-two hours as a maximum to probably twenty-four hours as a maximum instead of a minimum, in all cases.

The above experiments having served to show the minimum percentage of gas necessary to effect certain disinfecting results and the minimum time necessary to arrive at these same facts, it would now be well to consider the means for the practical application of sulphur dioxide as a disinfecting agent.

Several methods may be employed. Let us commence with the presumption that we desire to obtain a 5 per cent atmosphere in a given space. How can this be arrived at? As has been mentioned heretofore, there are numerous methods, the burning of sulphur, the production of sulphur dioxide by the action of sulphuric acid upon either copper or sulphur, and it has also been noted that under the influence of pressure or low temperatures, or the two combined, sulphur dioxide may be reduced to a liquid condition readily expansible by the application of heat. Therefore, the first method may be given as the use of liquefied sulphur dioxide in such quantities as to obtain the percentage required. It must be borne in mind here (having reference to the atomic weights of sulphur, oxygen and sulphur dioxide) that 1 pound of sulphur will produce 2 pounds of sulphur dioxide. Therefore, reversing the proposition, 2 pounds of liquefied sulphur dioxide must be used in lieu of 1 pound of sulphur. This method is efficient and rapid, but very expensive, and, except under certain conditions, may be eliminated from our consideration of practical quarantine measures. Neither is it worth while, in this connection, to give consideration to either of the other two methods of the treatment of either sulphur or copper by sulphuric acid, as they entail the use of heat and apparatus more or less complicated. In addition to which, it is a procedure not free from danger for the uninitiated to subject concentrated sulphuric acid to the action of heat. Terrific accidents and horrible burns might easily result. But a means easy and effectual still remains to us. That is the combustion of sulphur in the presence of atmospheric oxygen.

Taking into consideration the actual weight of a given number of cubic inches of sulphur dioxide, we find that disregarding temperature and barometric pressure, and presuming that our sulphur is free from contaminations or impurities, we can obtain about 1.15 per cent of sulphur dioxide by the combustion of 1 pound of sulphur in a space of 1,000 cubic feet. Sulphur, however, is seldom pure, containing impurities in the nature of sulphate of lime and sand, and a portion of it being always oxidized to the formation of ill-defined compounds. Again, all gases have a very regular rate of expansion and a constant factor is equivalent to $\frac{11}{3000}$ for each degree centigrade from zero up. It has been noted by Surgeon Carter, M. H. S., that the holds of vessels during the process of combustion of sulphur sometime reaches 140° F., or 60° C. Presuming, therefore, on a normal temperature of 22° C. we have ranges of temperature from 22° to 60° C., or a range of 38°, giving an expansion of gas about equivalent to $\frac{4}{30}$ of the entire mass. Taking this, we have 1.03 as the obtainable percentage under normal conditions of temperature, and making allowance for the impurities noted as existing in sulphur, it might be said that in round numbers 10½ pounds of sulphur can be counted on as producing 10 per cent sulphur dioxide in 1,000 cubic feet of space. To obtain 5 per cent, therefore, is simply to use one-half or 5¼ pounds. Of course, it would be prudent to allow for wastage or for imperfect combustion, and these factors one must decide for himself. It has been suggested that 20 per cent be allowed for these sources of error.

As has been seen, the presence of moisture is necessary to an effectual germicidal power on the part of sulphur dioxide. In other words, that sulphur dioxide must be converted into sulphurous acid. It is comparatively easy to arrive at the amount of water necessary for this. The atomic weight of sulphur dioxide as compared with sulphurous acid is as 64 to 82; in other words, about 20 per cent of the weight of sulphur used should be allowed for water to be volatilized or added to produce a proper hydration. Therefore, one-fifth pound, theoretically, of water should be volatilized or added for each pound of sulphur burned. Many ways suggest themselves of effecting this result. The water might be applied in the form of steam after the combustion of the sulphur. It might be added after the combustion of the sulphur in the form of a finely divided spray, or it might be vaporized by the heat generated in the combustion of the sulphur itself. The latter method is the one that will commend itself for practical use. Of course, it might be possible to evaporate a given quantity of water and turn the resulting steam into the apartment or hold filled with sulphur dioxide, but this would require a special apparatus. The same might be said of the production of the spray, but it would require a spray of considerable power to reach to all parts which have been penetrated by the sulphur dioxide, and, as the process would have to be conducted by faith rather than by sight, it is not a commendable practice. On the contrary, the vaporization of water by the heat engendered in the burning of the sulphur is, so to speak, an automatic process.

Let the sulphur be burned in shallow pots of iron, nothing being better than the old-fashioned Dutch oven for this purpose, and let each of these containers stand in a larger vessel containing water. As the iron of the oven becomes hot, water will be vaporized and rising around the fumes of the burning sulphur, union will at once take place and nascent sulphurous acid will be the result.

Again, allowance must be made for unavoidable losses or defects. While about one-fifth would be about the theoretical requirement, let one-half pound of water be vaporized for every pound of sulphur used.

A point of much importance, which should be mentioned, is that the vessels containing the burning sulphur should not rest at the lowest point of the apartment or hold undergoing disinfection, but, as recommended by Surgeon White, the pots should be elevated in the holds of vessels on piles of ballast, which would raise them a considerable distance above the floor of the hold of the ship undergoing disinfection or the floor of the apartment which it is desired to purify. The reason for this is obvious upon consideration. Hot gases ascend and naturally fill the upper portions of the apartments; on cooling, they descend and fill the lower strata of the hold or room. Here the flame extinguishing effect of sulphur dioxide comes into play, and it is quite possible that the flames of the burning sulphur would be extinguished before the oxygen of the atmosphere was exhausted by chemical union with the sulphur. The object to be attained is very simple; to convert all of the oxygen of the contained atmosphere of the hold or apartment into sulphur dioxide by union with burning sulphur. Bearing this in mind, methods for accomplishing this end will readily suggest themselves to anyone of ordinary intelligence, certainly to anyone who has had practical experience in the matter of ship or room disinfection.

The mention of another practical point will fittingly bring this article to a close. It has come under the observation of the writer that in some places where the "pot method" of disinfection of ships was practiced, it was the habit to employ one large vessel, a caldron or wash boiler, for the combustion of the sulphur. This is wrong, for, should the flame be extinguished by the effect of the gas, the whole process would necessarily have to be gone over. If the sulphur is divided among a considerable number of smaller containers the greater part of this danger is obviated and, there being more sources of supply, the uncertainty which always surrounds the practical diffusion of gases is neutralized.

It is therefore recommended that the combustion of sulphur should be effected in such a manner that no vessel used for the combustion should contain more than 30 to 40 pounds of the sulphur. This sulphur, too, should be in a state of fine division, and ignition should be obtained by using a liberal quantity of alcohol to start the fire in each pot.